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SEPARATION OF OXYGEN FROM SEAWATER BY MEMBRANE PERMEATION

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I. INTRODUCTION AND SIGNIFICANCE OF THE PROBLEM

A reliable and compact system able to extract dissolved oxygen from seawater is required for a number of naval applications. This proposal describes the application of a membrane process called pervaporation to the problem of oxygen separation. Over the past four years, we have developed a pervaporation process for extracting dissolved organic solvents from dilute aqueous feed streams. With some modifications, the same membranes and membrane systems can be used to extract oxygen from seawater. Seawater containing dissolved air is brought in contact with one side of a selective membrane. A partial vacuum is applied to the other side of the membrane and this produces a flow of water vapor, oxygen, nitrogen and carbon dioxide across the membrane. The flow of each component across the membrane is determined by the partial pressure difference and the permeability properties of the membrane. As will be shown in this report, it is possible to operate the membrane such that only oxygen is extracted.

Two uses for the oxygen extracted from seawater have been examined. The first application is the production of oxygen enriched air for submarine life-support systems. Currently, this oxygen is produced by electrolysis of water. The second application is the production of oxygen as an oxidant for a fuel cell. Fuel cells are used as power sources for submerged sensor stations. A water-oxygen circulation system would reduce the bulk and extend the lifetime of such a system. The utility of a membrane system to these two applications is described in more detail in Section VI of this report.

II. BACKGROUND

A. THE PERVAPORATION PROCESS

The theory of pervaporation has been described extensively in the literature, and will not be covered in detail here.¹⁻³ In essence, pervaporation is a diffusion-controlled membrane process, used to separate one or more volatile dissolved components from a liquid feed mixture. Water and dissolved gases or vapors permeate the membrane at a rate determined by their relative volatilities and their ability to permeate the membrane. The rate-controlling step is assumed to be diffusion through the membrane under a concentration gradient. The overall separation factor, β_{pervap} , depends on the intrinsic selectivity of the membrane, defined as the ratio of the permeabilities of the components, and on the partial pressure differences of the components on the feed and permeate sides of the membrane. The full selectivity of the membrane is only utilized when the partial pressure difference is maximized. Thus, in order to get a good separation of components in a pervaporation process, it is important to use a membrane material with high intrinsic selectivity for the components to be separated, and to operate the system with the largest practical partial pressure difference through the membrane. The process in its simplest form is shown in Figure 1.

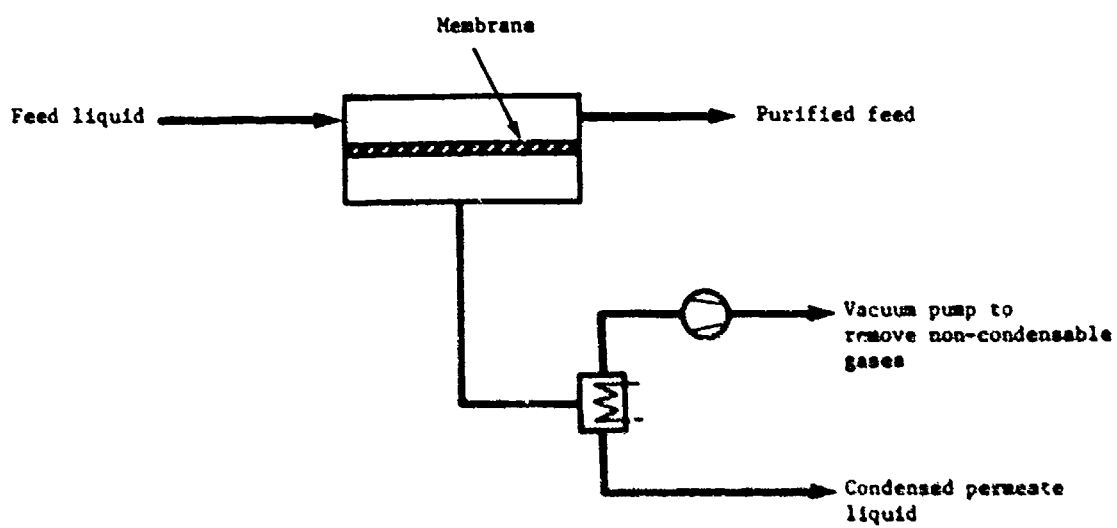


Figure 1. Schematic of pervaporation process.

In a practical system, a liquid mixture contacts one side of a membrane and the permeate is removed as a vapor from the other side. Transport through the membrane is induced by maintaining the partial vapor pressure on the permeate side lower than the partial pressure on the liquid side. This partial pressure difference can be achieved in several ways, most economically by cooling the permeate vapor, causing it to condense. Condensation of the permeate vapor spontaneously generates the permeate vacuum required. Pervaporation units are equipped with small vacuum pumps to remove noncondensable gases (primarily dissolved air).

In this pervaporation process the desired product is the noncondensable gas oxygen. The amount of dissolved oxygen in water is actually very low: 8-7 ppm by weight, if the water is fully saturated with air. This low oxygen concentration substantially affects the performance of the process. Most importantly, the water feed flow rate to the membrane system has to be large in order to provide enough oxygen to be extracted. Thus, the feed flow rates used in the extraction process will be much larger than those normally encountered in pervaporation applications.

B. MEMBRANE AND MODULE TECHNOLOGY

The heart of MTR's pervaporation separation technology is our ability to produce high flux, high selectivity, multilayer polymer membranes. The multilayer membrane structure consists of a tough, open microporous polymer layer that provides strength, and an ultrathin dense polymer coating that is responsible for the separation properties. The MTR composite membrane structure is shown schematically in Figure 2. Over the past six years, the company has developed the technology to produce these membranes defect-free, in rolls 40 inches wide and 100-200 yards long. The membranes have been tested at pressure differences up to 500 psig and proved to be stable. The anticipated maximum operating pressure for oxygen extraction systems is expected to be well over 500 psig. Thus, in an eventual follow-on program, the membrane will have to be tested at higher pressures. Membrane stability at the higher pressures is not expected to be a problem, however.

The composite membranes are fabricated into spiral-wound modules of the type illustrated in Figure 3. In operation, feed liquid enters the module and flows between the membrane leaves. The organic solvent components of the feed, as well as dissolved air, go through the membrane more readily than water. The fraction of the feed that goes through the membrane spirals inward to a central permeate collection pipe. The remainder of the feed flows across the membrane surface and exits as the residue. These membrane modules can be connected in a serial or parallel flow arrangements to meet the capacity and separation requirements of any particular separation.

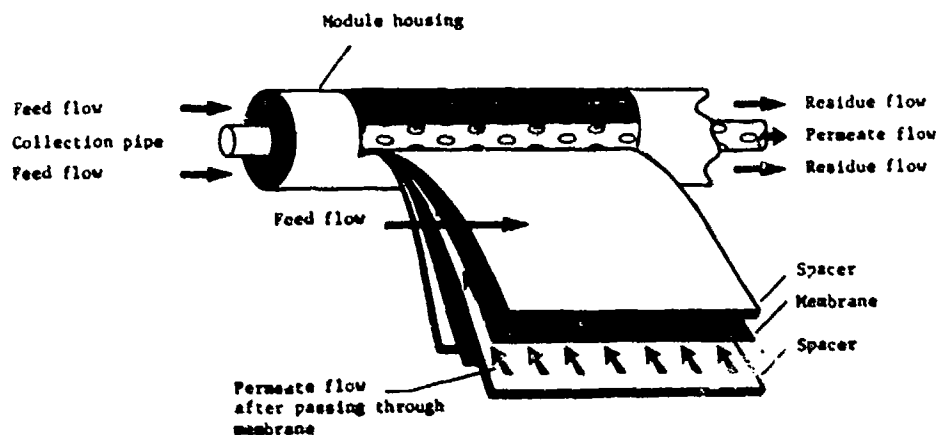


Figure 2. Schematic of MTR composite membrane. MTR produces these membranes in rolls 100-200 yards long and 40 inches wide.

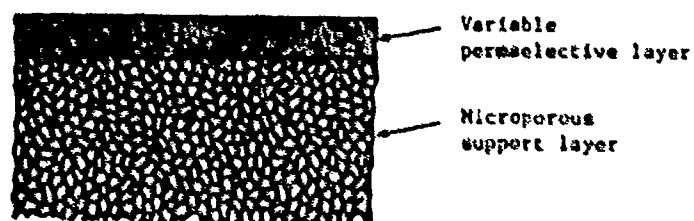


Figure 3. A spiral-wound membrane module. MTR produces modules with membrane areas ranging from 0.3 m² for laboratory modules to 6-m² commercial-sized modules.

III. PHASE I OBJECTIVES

The overall goal of this program was to demonstrate the feasibility of using pervaporation to remove dissolved oxygen from seawater. Specific tasks involved building and operating a laboratory-scale test unit and using the experimental results obtained with this unit in a preliminary system analysis aimed at two applications: (a) oxygen for fuel cells, and (2) oxygen for life support.

IV. EXPERIMENTAL METHODS

A. MODULE PREPARATION

Composite membranes were prepared using MTR's standard casting and coating procedures. Two permselective materials were used. One had higher oxygen-over-nitrogen and carbon dioxide-over-nitrogen selectivities than the other, but was less permeable. One high-selectivity and two high-flux membranes of different thicknesses were prepared. Each membrane was then incorporated into a spiral-wound module. An open spacer type was selected for the feed channel spacer to reduce the feed-to-residue pressure drop in the modules, as the experiments were expected to be carried out at feed flow rates much higher than normally encountered in standard pervaporation applications. Table 1 compares the oxygen and nitrogen permeation properties of the three modules. All three modules had an oxygen-over-nitrogen selectivity equal to the selectivity of the membrane before it was incorporated into the module. This indicates that the modules were free of defects. As can also be seen from Table 1, the oxygen flux through module #1 was about three times higher than that through module #2. The permselective membrane layer in module #1 was therefore about three times thinner than the permselective layer in module #2.

Table 1. Permeation Properties of Spiral-Wound Modules used in Oxygen Extraction Experiments

Membrane Area: 5.6 m²

Module	Permselective Material	Oxygen Permeation Rate* (L(stp)/min)	Selectivity (oxygen/nitrogen)
1	High flux	7.0	2.2
2	High flux	2.5	2.1
3	High selectivity	1.2	3.7

*At 1 psi pressure difference across the membrane.

B. OXYGEN EXTRACTION EXPERIMENTS

The experimental apparatus for measuring the oxygen extraction rate from water is shown in Figure 4. A photograph of the system is shown in Figure 5. The feedwater was continuously aerated with atmospheric air to saturate the water with oxygen, nitrogen and carbon dioxide. The water was pumped through a filter to remove air bubbles, and then passed through the membrane module. The residue stream exiting the module was returned to the tank. Flow through the membrane was achieved by maintaining a reduced pressure on the permeate side of the membrane. The water vapor in the permeate stream was condensed in the cooler and the noncondensable gases, i.e., oxygen, nitrogen and carbon dioxide, were removed via the vacuum pump. The composition of the gas stream exiting the vacuum pump was analyzed with a gas chromatograph. The dissolved oxygen concentration in the feed and residue streams was measured with a dissolved oxygen meter. In all experiments, good agreement was found between the amounts of oxygen removed from the water and the amount of oxygen present in the permeate gas stream.

For simplicity, experiments were carried out using regular tap water. For some experiments we used an artificial seawater mixture, prepared by adding a powder, "Instant Ocean" (Aquarium Systems, Mentor, OH), to the tap water. The added salts slightly changed the equilibrium concentrations of oxygen, nitrogen and carbon dioxide in water. However, because the salts are nonvolatile, they did not permeate the membrane.

V. RESULTS AND DISCUSSION

A. OXYGEN EXTRACTION RESULTS

Oxygen extraction experiments were carried out with three modules containing three different membranes: (1) a high-flux thin membrane, (2) a high-flux, thicker membrane, and (3) a high-selectivity membrane. All experiments were carried out using the apparatus described above, and the operating conditions given in Table 2. The feed flow rate was varied over the range 1-20 gallons per minute (gpm). These are higher flow rates than are typically used with pervaporation systems for standard applications, which normally operate at 0.5 to 5 gpm feed flow rate per individual module.

Table 2. Conditions During Oxygen Extraction Experiments

Feed temperature:	20°C
Condenser temperature:	5°C
Feed composition (air saturated water):	6.5 cm ³ (STP)O ₂ /L water 12.4 cm ³ (STP)N ₂ /L water 0.3 cm ³ (STP)CO ₂ /L water
Permeate pressure:	1 cmHg
Feed flow rate:	1- 20 gpm

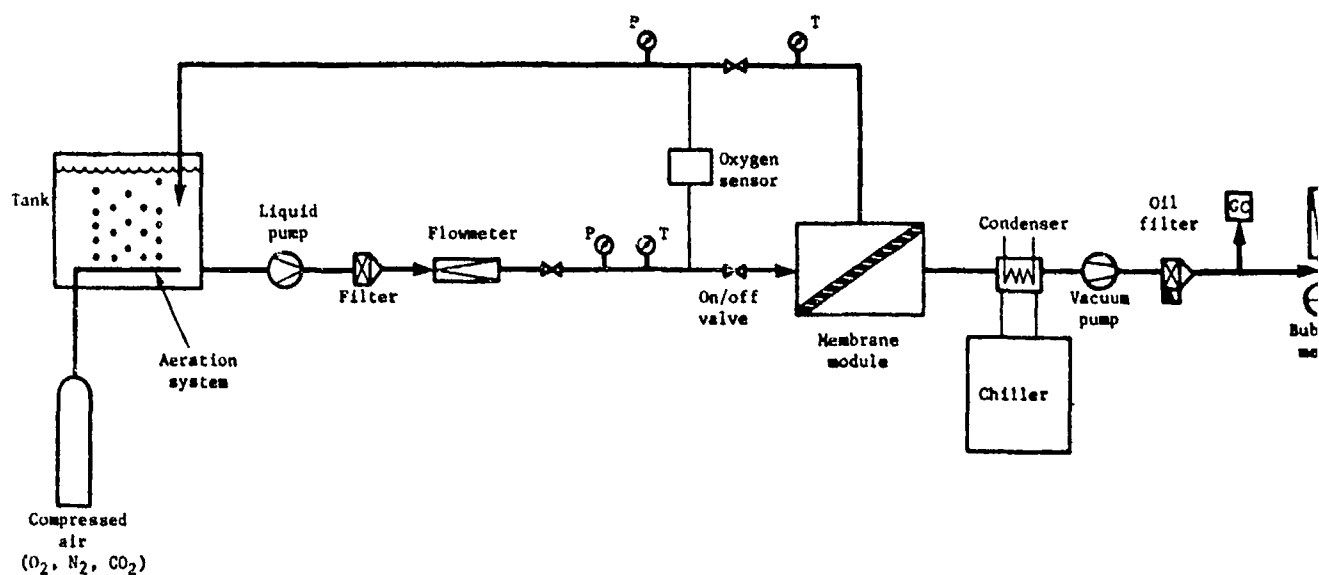


Figure 4. Schematic of experimental apparatus for measuring the oxygen extraction rate from seawater by pervaporation.



Figure 5. Photograph of the experimental set-up for measuring the oxygen extraction rate from water.

The modules were able to extract approximately 40% of the gas dissolved in the feed, producing a permeate stream of oxygen-enriched air at a rate of 150-450 cm³/min. The results are shown in more detail in Figures 6, 7 and 8. Figure 6 shows the composition of the permeate gas as a function of the feed flow rate for module #1, the higher-flux module and module #3, the high-selectivity module. Data for module #2 containing the thicker membrane are not shown. However, modules #1 and #2 gave essentially identical results. The composition of the permeate gas was the same for all these modules and was independent of the feed water flow. The permeate gas composition (33% O₂, 66% N₂ and 1.3% CO₂) closely resembles the composition of air dissolved in water (see Table 2).

The oxygen permeate flow rate is shown as a function of the feed flow rate in Figure 7. The oxygen extraction rate is roughly proportional to the feed flow rate and is the same for modules #1 and #2, even though the membrane in module #2 is about three times less permeable than the membrane in module #1. The oxygen permeate flow rate measured for module #3 is about 25% lower than that obtained with the other two modules. Figure 8 gives the oxygen removal from the feed stream as a function of the feed flow rate. Oxygen removal is defined as the percentage of the oxygen present in the feed stream that is removed from the feed stream via the membrane. Figure 8 shows that the oxygen removal decreases slightly with increasing feed flow rate, and that the amount of oxygen removed is independent of the membrane type used.

Based on the results shown above, it appears the air production rate can be increased by increasing the feed water flow rate. However, increasing the feed water flow rate requires a greater pressure to force the water through the modules. We therefore measured the feed-to-residue pressure drop as a function of feed water flow rate. The results are shown in Figure 9. From these data, the energy requirement per cm³(STP) oxygen produced can be calculated as a function of feed flow rate.

The data shown in Figure 7 and 8 were obtained with oxygenated tap water. A few comparative experiments were performed with artificial seawater. Table 3 summarizes the results, including those obtained with the artificial seawater mixture. The oxygen extraction rate is 10 to 15% lower in the case of seawater because saline water has a lower solubility for gases than pure water. Table 3 also shows that the extracted amount of potable water is independent of the module feed flow rate.

Table 3. Oxygen Extraction Performance Data Obtained with a Spiral-Wound Membrane Module at Two Feed Flow Rates

Permeate Flow Rate	Module Feed Flow Rate			
	(1 gpm)		(20 gpm)	
	Tap water	Seawater	Tap water	Seawater
Oxygen (L/h)	0.66	0.58	11	9.2
Air (L/h)	22	19	36	30.6
Water (g/h)	0.4	0.4	0.4	0.4

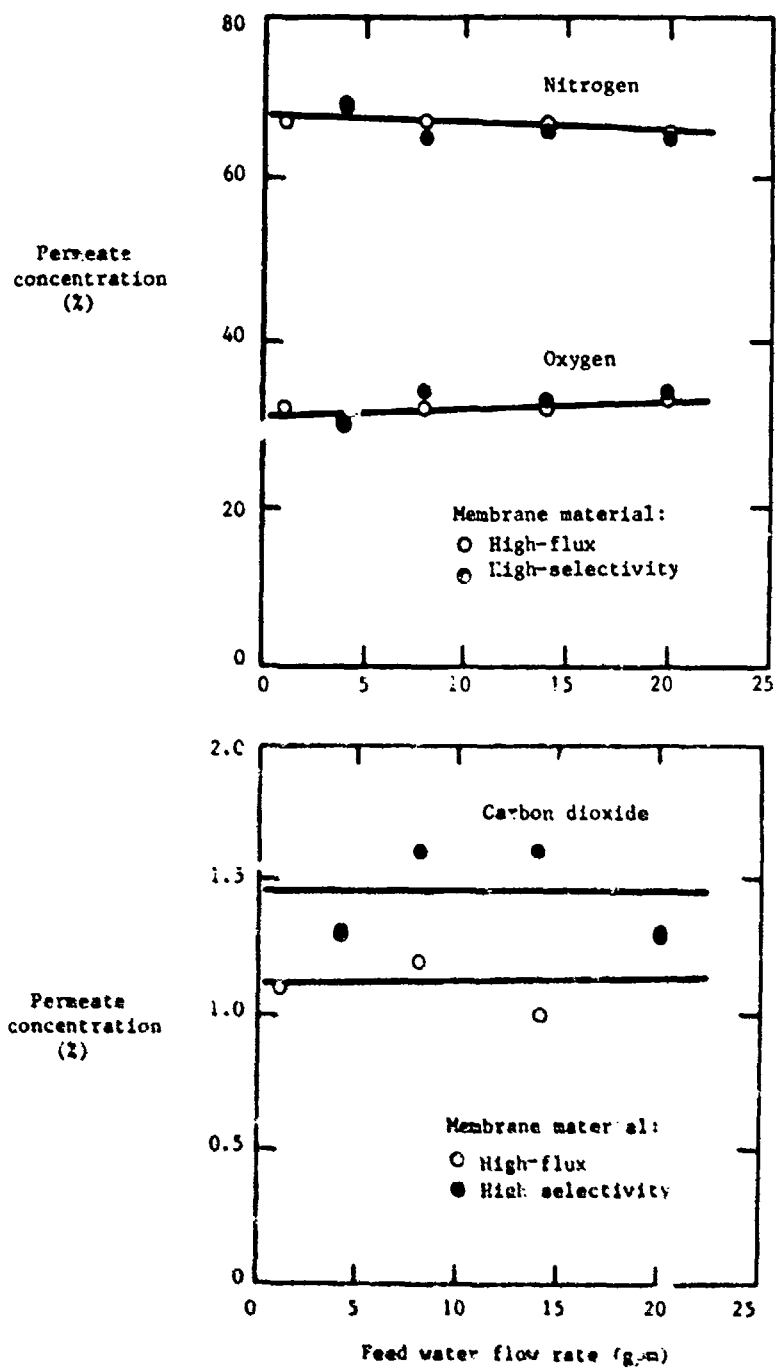


Figure 6. Composition of the permeate gas as a function of the feed flow rate for two spiral-wound modules with different permselective membrane materials.

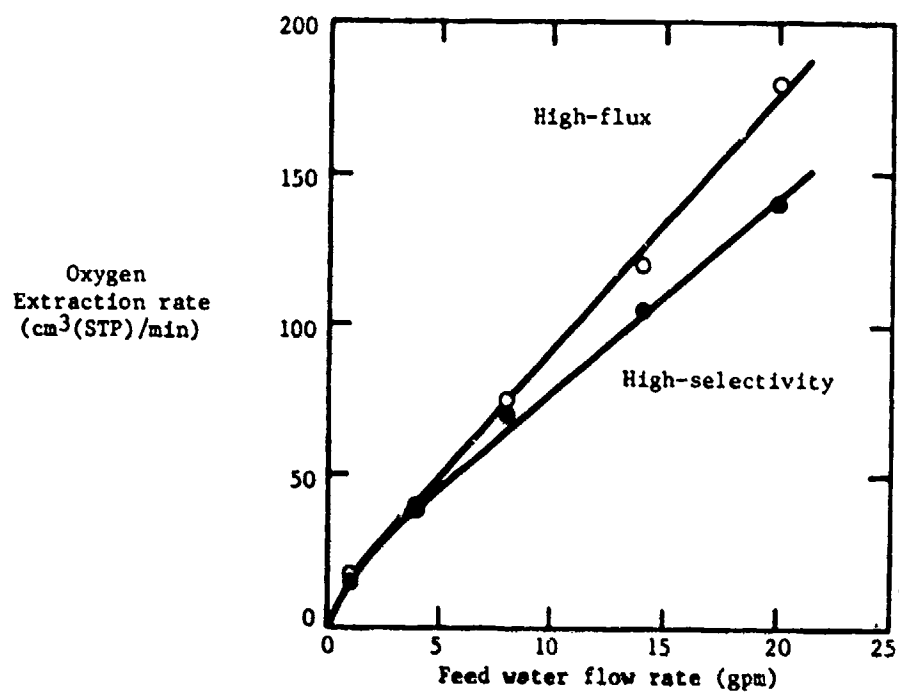


Figure 7. Oxygen extraction rate per six-inch module as a function of feed water flow rate at room temperature. (Membrane area = 5.6 m².)

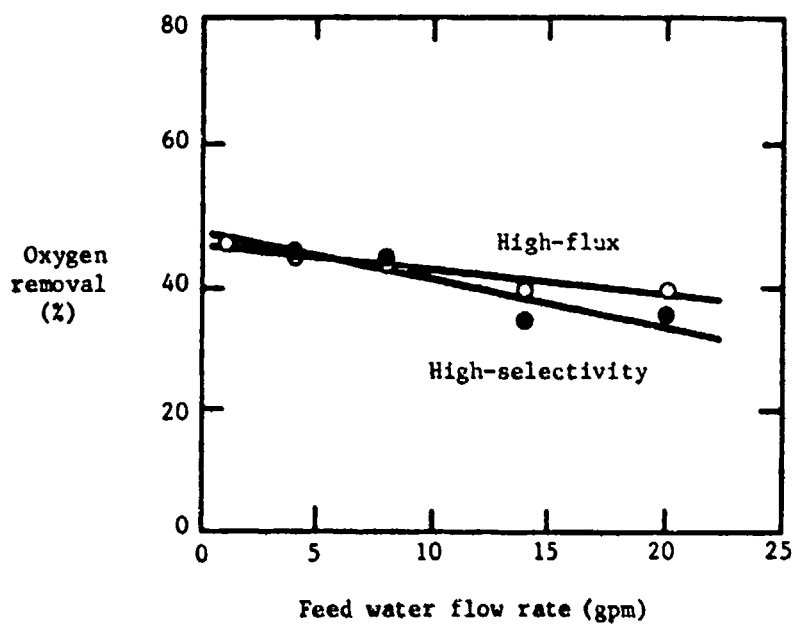


Figure 8. Oxygen removal as a function of feed water flow rate at room temperature. (Membrane area = 5.6 m^2 .)

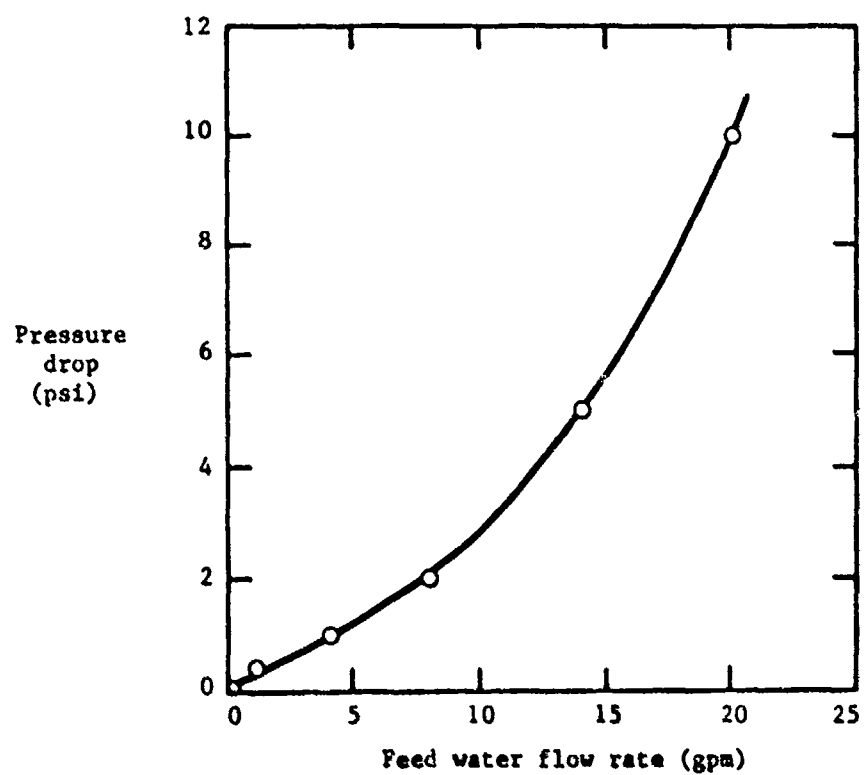


Figure 9. Pressure drop across pervaporation module as a function of feed water flow rate.

B. INTERPRETATION OF RESULTS

The module experiments showed that the permeate gas composition, and the oxygen removal from the feed achieved by the membrane system, were both independent of the nature of the membrane, and essentially independent of the feed flow rate. The permeate gas flow rate was found to be proportional to the feed flow rate. These results are in sharp contrast to those normally expected from a pervaporation system. The differences are caused by the very low concentration of dissolved oxygen in seawater, which produced a boundary layer resistance next to the membrane surface. The effect of this boundary layer on oxygen extraction from seawater can be understood with reference to Table 4, which lists five features determined experimentally in the oxygen extraction experiments and five corresponding features of a standard pervaporation process.

Table 4. Characteristic Features of the Oxygen Extraction Process in Comparison with a Standard Pervaporation Process

Oxygen Extraction (oxygen from water)	Pervaporation (organic from water)
Permeate composition independent of membrane properties	Permeate composition depends on membrane properties
Permeate flow rate independent of membrane properties	Permeate flow rate depends on membrane properties
Permeate composition independent of feed flow rate	Permeate composition depends on feed flow rate
Permeate flow rate of preferentially permeating component (oxygen) proportional to feed flow rate	Permeate flow rate of preferentially permeating component (organic) increases slightly with feed flow rate
Percentage of preferentially permeating component (oxygen) removed from the feed minimally dependent on feed flow rate	Percentage of preferentially permeating component (organic) removed from the feed decreases markedly with feed flow rate

The differences in performance arise from the different mass transfer characteristics encountered in the oxygen extraction process. As mentioned in Section II.A., the transport of vapors and gases in pervaporation applications is generally considered to be controlled by diffusion across the membrane under a concentration gradient through the membrane. However, the transport of gases in the oxygen extraction process is controlled by diffusion across the stagnant liquid boundary layer in the feed water adjacent to the membrane. The situation is shown graphically in Figure 10. The boundary layer is a thin film of stagnant water adjacent to the membrane. The thickness of the boundary layer is mainly determined by the feed flow rate and decreases with increasing feed flow rate. Typically, the boundary layer is several hundred microns thick, which is very thick compared to the permselective membrane layer. Because the membrane is very efficient in removing the dissolved gases from the boundary layer, the boundary layer contains considerably less dissolved gas than the bulk of the feed liquid. Thus, as is shown in Figure 10, a concentration profile develops in the boundary layer. The boundary layer thus forms an additional resistance to gas permeation, a phenomenon known as concentration polarization. If concentration polarization occurs in a membrane process, the performance of the process becomes relatively independent of the membrane properties and depends almost exclusively on the thickness of the boundary layer. The boundary layer thickness is in turn controlled by the turbulence in the feed water or by the feed water flow rate through the module. This is exactly the case in the oxygen extraction process, as the data in Table 4 show. Because the oxygen extraction rate is limited by the diffusion step in the boundary layer, the module's performance is only marginally influenced by the membrane type. The membrane is basically acting as a contactor, or a physical barrier between the two phases, and does not play an active role in the separation step. The performance of the system in terms of oxygen flow rate can be increased by making the boundary layer thinner, thereby increasing the rate of diffusion across the layer. This is achieved by increasing the feed flow rate.

VI. SYSTEM DESIGN AND ANALYSIS

The oxygen extraction experiments showed that a membrane process is capable of removing and recovering oxygen from seawater. In this section, we will discuss how a system to extract oxygen from seawater would be used in two applications: (1) oxygen for fuel cells in submerged sensor stations, and (2) oxygen for life support in a submarine. These applications have very different requirements, summarized in Table 5. The most important difference between the applications is that the power consumption is relatively unimportant for submarine life support systems, but is a major concern in the fuel cell application. Another difference is that fuel cells can utilize oxygen at low partial pressure, i.e., at less than 21% oxygen and at subatmospheric pressure levels, whereas in the life support application, oxygen is usable only at partial pressures over 0.21 atm. The amount of carbon dioxide extracted from the seawater is also a concern in a life support application because even relatively low concentrations of carbon dioxide will make the submarine atmosphere unbreathable. Fuel cells, however, can be run with comparatively high carbon dioxide content in the oxygen stream. In both applications, the overall volume and weight of the oxygen extraction system are important.

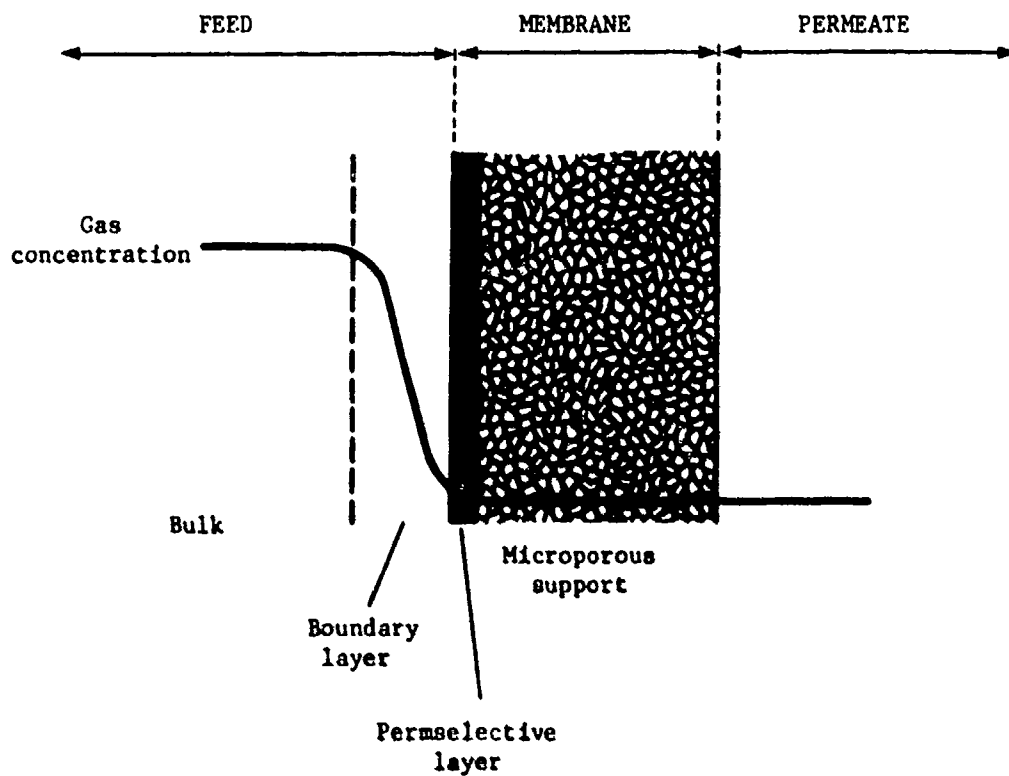


Figure 10. Concentration profile of dissolved gases (oxygen, nitrogen and carbon dioxide) in oxygen extraction experiments.

Table 5. System Design and Performance Requirements for Membrane System to Extract Oxygen from Seawater

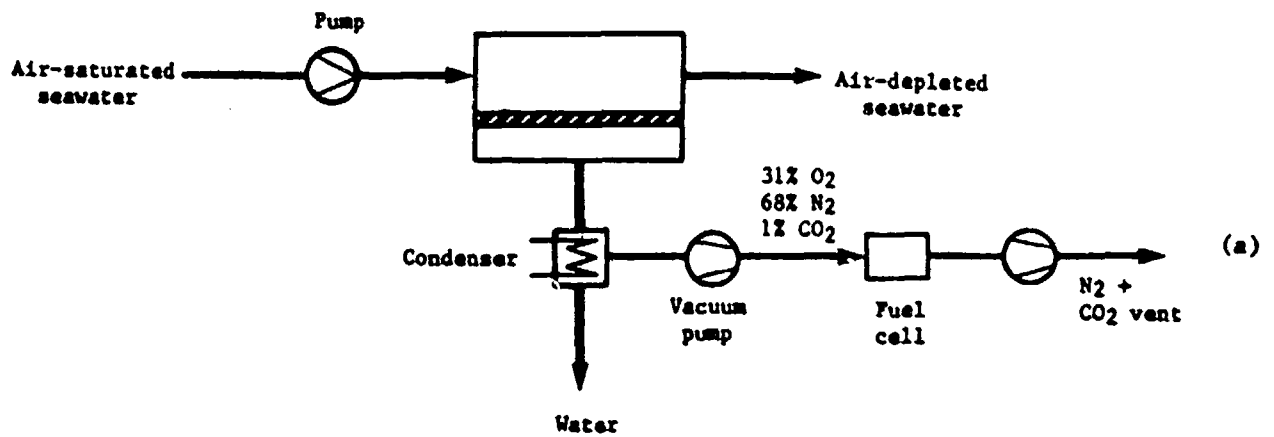
<u>System Design Parameters</u>	<u>Life Support</u>	<u>Submerged Fuel Cell</u>
Volume + weight	important	-
Power consumption	-	important
Noise	important	important
<u>System Performance</u>		
Required oxygen concentration	>20% preferably >10%	-
Permeate carbon dioxide concentration	important	-
Permeate pressure of permeate gas mixture	important	-

A preliminary system design analysis was performed for the two applications. The fuel cell application is promising. The oxygen for life support application is less promising, although possibly still feasible. A discussion of both applications follows.

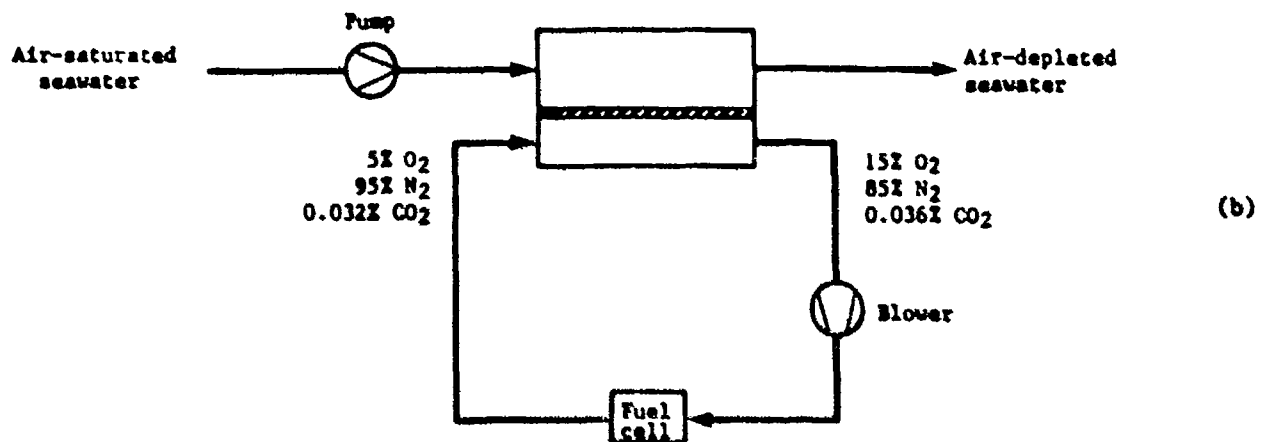
A. OXYGEN FOR SUBMERGED FUEL CELLS

Submerged sensor stations require a power source which will continuously deliver 1 to 2 kW for several hundred days without any maintenance. Fuel cells are capable of meeting these requirements. The fuel is hydrogen, which is stored in the station as pressurized hydrogen or a metal hydride. The oxidizer is oxygen, which can be stored in the station, but preferably will be extracted from the surrounding seawater. A 1 to 2 kW fuel cell will need 5 to 10 liters per minute of pure oxygen.⁴ In this section, we describe an oxygen extraction system capable of generating 10 liters of oxygen per minute, to supply a fuel cell producing 2 kW.

Two possible oxygen extraction system designs are illustrated in Figure 11. The vacuum-mode system shown in Figure 11(a) resembles the experimental set-up used in this program. In the vacuum-mode system, a vacuum pump is used to maintain the oxygen partial pressure in the permeate gas under the equilibrium pressure of the oxygen dissolved in the seawater. Nitrogen and carbon dioxide, which permeate the membrane along with the oxygen, must be disposed of and this would be done by compressing these gases to the hydrostatic pressure of the seawater and venting them. The power required for the compression step could be substantial and would be detrimental to the energy efficiency of the fuel cell.



Vacuum-Mode System



Sweep-Mode System

Figure 11. Two different system designs for an oxygen extraction system for fuel cell applications.

A second system, which we call a sweep-mode system, eliminates the need to vent gases, as well as the need for a vacuum pump. In this system, shown in Figure 11(b), a gas stream consisting of oxygen, nitrogen and carbon dioxide is continuously recirculated between the fuel cell and the permeate side of the membrane. The fuel cell consumes oxygen, thus lowering the oxygen content in the recirculation stream. The difference in oxygen partial pressure between the recirculated gas and the oxygen in the seawater feed produces a flow of oxygen across the membrane into the recirculation stream. A steady state will be reached when the amount of oxygen permeating the membrane is equal to the amount of oxygen consumed by the fuel cell. A similar steady state for nitrogen and carbon dioxide means that no nitrogen and no carbon dioxide will permeate the membrane. The steady-state total pressure of the sweep stream will typically be under 76 cmHg, and is 66.7 cmHg, for example, in Figure 11(b).

The power demands of the extraction system operating in sweep mode are mainly determined by the energy needed to pump the seawater through the membrane modules. The lower the seawater flow rate per module, the less horsepower will be required. However, as was shown in Section V, the amount of oxygen extracted per module decreases with decreasing flow rate. A balance must therefore be made between membrane area and energy consumption. Table 6 gives system characteristics for three possible systems. Two of these systems, A and B, are based on the experimental data presented in this report; the third, System C, is hypothetical. System A assumes a high transmembrane seawater flow rate, and therefore requires fewer membrane modules and occupies a smaller volume. To achieve this high flow rate, the system requires more power to drive the pumps than the fuel cell generates, and is thus not feasible. System B assumes a more modest seawater flow rate, but consequently requires a ten-fold increase in the number of modules compared with System A. The system would use only 25% of the power generated by the fuel cell, but is very large and heavy. System C is the preferred alternative. This system, which was not developed during this Phase I program, but which could form the basis of a Phase II study, combines the module array of System A with seawater flow rate of System B. This arrangement would be possible by modifying the module design to reduce the pressure drop across the module between the feed and residue streams. This would have the effect of reducing the energy requirements of the system 50-100 fold. We believe that this level of improvement in module performance could be achieved by modifying the module design, principally by changing the type of feed spacer and/or the feed channel length. The modules used in this program were based on our standard pervaporation design and were not tailored specifically to the unique needs of this application. The improved system would be an acceptable source of oxygen for a fuel cell in a submerged sensor station.

Table 6. Comparison of Module and Power Requirements for Three Oxygen Extraction Systems Delivering 10 L/min Pure Oxygen

System	Seawater Flow Rate (gpm)	Number of Modules (m^3)	Volume of Modules (kW)	Power Required for Pumps
A	1,100	56	2	30
B	600	600	21	0.5
C	600	56	2	0.3-0.6

B. OXYGEN FOR LIFE SUPPORT

The second application of a seawater-oxygen extraction system is to supply breathable air for submarines. Nuclear-powered submarines remain submerged for several months and thus require oxygen generation systems to sustain their crews. Present systems produce oxygen from water by electrolysis. Coproduced hydrogen is stored or vented. Electrolysis consumes large quantities of electrical energy, but electricity is plentiful aboard a nuclear-powered submarine. However, an oxygen generation system that would eliminate the handling and storage of hydrogen would be of interest.

An oxygen extraction design similar to the one shown in Figure 11(b) could be used to generate oxygen for life support. The system in Figure 11(b) produces a permeate gas stream at slightly less than atmospheric pressure, with an oxygen content and partial pressure too low for direct use in a life-support system. For life-support, oxygen would have to be generated at a partial pressure over 0.21 atm and consequently a second membrane stage would be necessary. A conceptual design is shown in Figure 12. This two-stage, sweep-mode system could produce approximately 30% oxygen at normal pressure. No nitrogen would be extracted by virtue of the sweep mode. The sweep stream would also cause at least part of the carbon dioxide produced by respiration to diffuse in the reverse direction into the seawater. The system required to produce oxygen for submarine life support would be larger and more complicated than systems producing oxygen for fuel cells. We estimate that the vacuum pump would need at least one hp per crew member and this would raise concern about the noise level generated by the system.

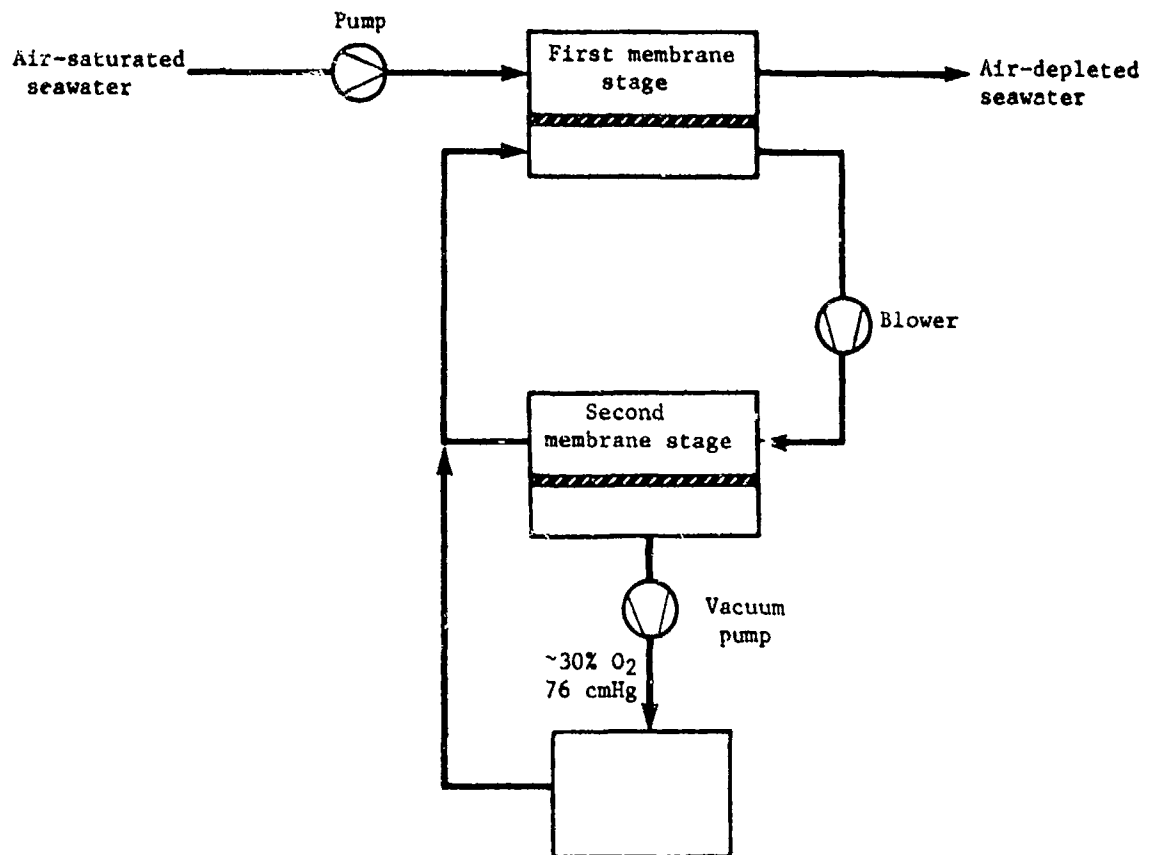


Figure 12. Conceptual design of an oxygen extraction system for life support applications.

VIII. CONCLUSIONS

The experimental work performed has shown that a membrane system is capable of extracting dissolved oxygen from seawater. The membrane transports oxygen by simple diffusion and is capable of withstanding relatively large pressure differences. A preliminary system design analysis has shown that the system can be operated such that an equilibrium is reached where oxygen, but no nitrogen or carbon dioxide, is extracted from the seawater. This eliminates the need to compress and vent these gases. Two applications were considered, (1) oxygen for submerged fuel cells, and (2) oxygen for life support aboard submarines. The fuel cell application is considered the more promising.

The objectives of an eventual Phase II program would be to construct and operate a laboratory-scale oxygen extraction system operating in the sweep-mode. Oxygen would be continuously removed from the sweep stream, as is the case in the fuel cell application. An important goal of the Phase II program would be to develop membrane modules with a very low feed-to-residue pressure drop. This would increase the energy efficiency of the oxygen extraction system, a crucial concern in the fuel cell application.

REFERENCES

1. R.C. Binning, R.J. Lee, J.F. Jennings, E.C. Martin, "Separation of Liquid Mixtures by Permeation," Ind. & Eng. Chem. **53**, 45 (1961).
2. D.R. Paul, O.M. Ebra-Lima, "Pressure-Induced Diffusion of Organic Liquids Through Highly Swollen Polymer Membranes," J. Appl. Polym. Sci. **14**, 2201 (1970).
3. F.W. Greenlaw, W.D. Prince, R.A. Sheldon, E.V. Thompson, "Dependence of Diffusive Permeation Rates on Upstream and Downstream Pressure," J. Memb. Sci. **2**, 141 (1977).
4. Handbook of Batteries and Fuel Cells, D. Linden, Ed., page 42-1 to 42-11, McGraw-Hill, New York (1982).